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(54) Bleach activation.

(57) Bleach catalysts comprising a complex of formula (I)

$$[L\ Mn\ X_p]^z\ Y_q \qquad (I)$$

wherein Mn is manganese in the II, III or IV oxidation state, X represents a coordinating or bridging species; p is an integer from 1 to 3; Y is a counter-ion the type of which is dependent upon the charge z of the complex which can be positive, zero or negative; q = z [charge Y]; and L is a ligand which is a macrocyclic organic molecule.

EP 0 549 272 A1

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This invention relates to the activation of bleaches employing peroxy compounds, including hydrogen peroxide or hydrogen peroxide adducts which liberate hydrogen peroxide in aqueous solution, as well as peroxy acids; to compounds that activate or catalyse peroxy compounds; to bleach compositions including detergent bleach compositions which contain a catalyst for peroxy compounds; and to process for bleaching and/or washing of substrates employing the above mentioned types of compositions. In particular, the present invention is concerned with the novel use of a specific class of manganese complexes as effective catalyst for the bleach activation of peroxy compound bleaches.

Complexes having the general formula:

$$[L_n Mn_m X_p]^z Y_q \qquad (A)$$

wherein Mn is manganese which can be either in the II, III, IV or V oxidation state, or mixtures thereof; n and m are independently integers from 1-4; X represents a coordinating or bridging species; p is an integer from 0-12; Y is a counter-ion, the type of which is dependent upon the charge z of the complex; z is the charge of the complex and is an integer which can be positive, zero or negative; q = $^z/$[charge Y]; and L is a ligand being a macrocyclic molecule of general formula:

$$\boxed{D - (CR^1R^2)_t - \left[D - (CR^1R^2)_{t'} \right]_s}$$

wherein R¹ and R² can each be zero, H, alkyl, optionally substituted; and each D can independently be N, NR, PR, O or S wherein R is H, alkyl, aryl optionally substituted; have been described in EP-A-0,458,397 as effective catalysts for bleaching with peroxy compounds. Though this definition covers both mono- and polynuclear complexes the specification makes no reference to mononuclear manganese-complexes and preference is clearly given to multi-nuclear manganese complexes, particularly the dinuclear manganese complexes of the general formula (A) wherein both n and m are ≧ 2.

Applicants copending US Patent Application 798396 describes mononuclear manganese of formula

$$[L\,Mn^{IV}(OR)_3]\,Y$$

where Mn is manganese in the +4 oxidation state;
R is a C_1-C_{20} radical selected from alkyl, cycloalkyl, aryl, benzyl and radical combinations thereof;
at least two R radicals may also be connected to one another so as to form a bridging unit between two oxygens that coordinate with the manganese;
L is a ligand selected from a C_3-C_{60} radical having at least 3 nitrogen atoms coordinating with the manganese; and
Y is an oxidatively-stable counterion; and their use as bleach catalysts.

It has now surprisingly been found, however, that other mono-nuclear manganese coordination complexes of the general formula:

$$[L\,MnX_p]^z Y_q \qquad (I)$$

wherein Mn can be either in the II, III or IV oxidation state; X represents a coordinating species such as Cl^-, Br^- I^-, F^-, NCS^-, N_3^-, I_3^-, NH_3, NR_3, $RCOO^-$, RO^-,

$$R_3C\overset{\overset{O}{\|}}{C}CH\overset{\overset{O^-}{|}}{C}CR_3,$$

RSO_3^-, RSO_4^- in which R is hydrogen, alkyl, aryl, both optionally substituted, or $R'COO^-$ where R' is alkyl or aryl, both optionally substituted, OH^-, O_2^{2-}, O^{2-}, HOO^-, H_2O, SH, CN^-, OCN^-, S_4^{2-} and mixtures thereof; p is an integer from 1-3; z denotes the charge of the complex and is an integer which can be positive, zero or negative; Y is a counter-ion the type of which is dependent upon the charge z of the complex; q = $^z/$[charge Y]; and L is a ligand and being a macrocyclic organic molecule of the following formula:

$$\boxed{\left[NR^3 - (CR^1(R^2)_u)_t \right]_s}$$

wherein t is an integer from 2-3; s is an integer from 3-4; u is zero or one and R¹, R² and R³ are each independently selected from H, alkyl, aryl, both optionally substituted; with the proviso that when p is 3 and Mn is manganese in the IV oxidation state X cannot each be RO^-; can also be used as bleach catalysts for peroxy compounds in the same effective way as the dinuclear manganese complexes of EP-A-0,458,397 and EP-A-

0,458,398.

The choice of X is less crucial for the catalytic activity, but may be of importance for the physical properties of the complex, such as solubility and stability.

Preferred ligands are those in which t = 2; s = 3; u=1; R^1, R^2, R^3 are each independently H or CH_3, particularly wherein R^1 and R^2 are both H and $R^3 = CH_3$.

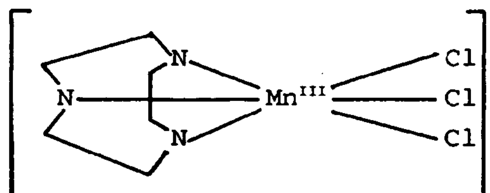
Examples of preferred ligands are:

1,4,7-triazacyclononane (TACN); 1,4,7-trimethyl-1,4,7-triazacyclononane (1,4,7-Me_3TACN); 2-methyl-1,4,7-triazacyclononane (2-Me-TACN); and 1,2,4,7-tetramethyl-1,4,7-triazacyclononane (1,2,4,7-Me_4TACN); and 1,2,2,4,7-pentamethyl-1,4,7, triazacyclononane (1,2,2,4,7-Me_5TACN); 2-benzyl-1,4,7-trimethyl-1,4,7-triazacyclononane; and 2-decyl-1,4,7-trimethyl-1,4,7-triazacyclononane.

The aforementioned ligands may be synthesised by the methods described in K Wieghardt et al., Inorganic Chemistry 1982, 21, page 3086 et seq, incorporated herein by reference.

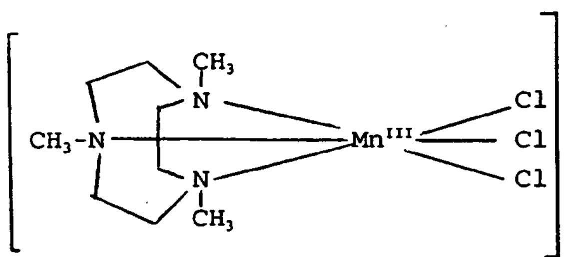
Examples of suitable complexes are:

(1)



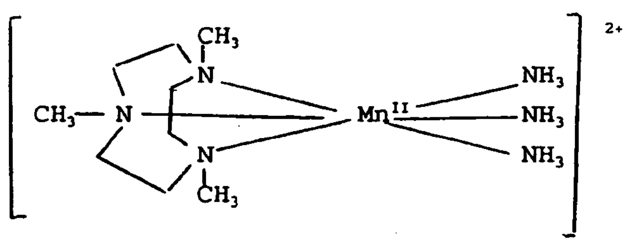
= [(TACN)$Mn^{III}Cl_3$]

(2)



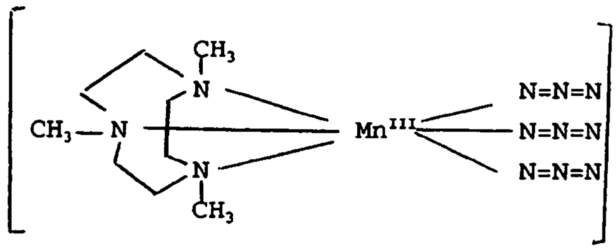
= [(1,4,7-Me_3TACN)$Mn^{III}Cl_3$]

(3)



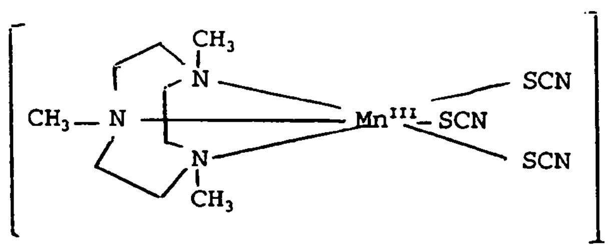
= [(1,4,7-Me_3TACN)$Mn^{II}(NH_3)_3$]$^{2+}$

(4)



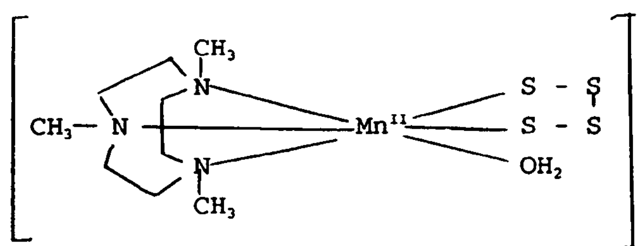
$= [(1,4,7\text{-}Me_3TACN)Mn^{III}(N_3)_3]$

(5)



$= [(1,4,7\text{-}Me_3TACN)Mn^{III}(SCN)_3]$

(6)



$= [(1,4,7\text{-}Me_3TACN)Mn^{II}S_4OH_2]$

(7) $[(1,4,7\text{-}Me_3TACN)\ Mn(AcAc)(EtO)]BPh_4$ where AcAc is acetylacetonate.

Some complexes usable as bleach catalysts of the invention were prepared and synthesized as illustrated below:

- Synthesis of Complex (4) and Complex (5):
  To a solution of $[Mn^{III}_2(\mu\text{-}O)(\mu\text{-}OAc)_2(1,4,7\text{-}Me_3TACN)_2](ClO_4)_2$, (0.5g in 30 ml ethanol), was added solid sodium azide (0.5g) or sodium thiocyanate at room temperature while stirring. Small red-brown crystalline material precipitated. (Yields: 0.3-0.4g).
  (K. Wieghardt et al, Inorg. Chim. Acta, 126,39 (1987))
- Synthesis of Complex (6):
  A solution of $Mn(OAc)_3.2H_2O$ (1g) and $1,4,7\text{-}Me_3TACN$ (1g) in methanol was stirred at room temperature

for 30 minutes under argon atmosphere, after which an aqueous solution of $(NH_4)_2S$ (2 ml;40%) was added. After reducing the volume to 15 ml under reduced pressure and standing for 24 hr in the refrigerator, pale yellow crystals formed, which were collected by filtration. Yield: 0.48g.
(K. Wieghardt et al, Inorg. Chim. Acta, 126,39 (1987).

- Synthesis of Complex (2)
  To a solution of $[Mn^{III}_2(\mu\text{-}O)(OAc)_2(1,4,7\text{-}Me_3TACN)_2](ClO_4)_2$, (1g in 20 ml CH_3CN) was added 10 drops of concentrated hydrochloric acid at room temperature. Yield: 0.25g.
  (K. Wieghardt et al, J. Am. Chem. Soc. 110,7398 (1988).
- Synthesis of Complex (3): $[MeTACN\ Mn^{II}(NH_3)_3](ClO_4)_2$:
  0.5g of 1,4,7-Me_3TACN was dissolved in 15 ml of methanol with 0.5 ml of ammonia under argon. To this solution, 1.0g of $Mn(ClO_4)_2$ in 15 ml of methanol under argon was added. The white precipitate was isolated under argon.
- Synthesis of Complex (7):
  0.5g of 1,4,7-Me_3TACN was dissolved in 25 ml of ethanol. Thereafter, 1.35g $Mn(AcAc)_3$ was added and the resulting mixture stirred for 30 minutes.
  To this was added 0.7g sodium tetraphenylborate dissolved in 20 ml of water. A yellow-green coloured precipitate formed. This was filtered off and dried in vacuo (Yield 1.4 g).
  (K Wieghardt et al, Z Naturforsch, 43b, 1184-1194, 1988).

Instead of using these neat crystalline materials the mononuclear manganese complexes of the invention may also be obtained and presented as a solution by adding a Mn-salt, such as $Mn(NO_3)_2$, to an acid solution of the ligand, e.g. 1,4,7-Me_3TACN, in water. The solution as obtained can be added to a bleaching solution containing a peroxycompound to give comparable results to those obtained with the isolated Mn-complexes.

The mononuclear manganese complexes of the present invention find particular application in bleach compositions and in bleach compositions.

Thus, according to another aspect of the invention there is provided a bleach composition comprising a peroxy compound, and a complex of formula (I) as hereinbefore defined. Preferably, the composition will also comprise a surface active material and detergent additives such as builders.

An advantage of the bleach catalysts of the invention is that they are hydrolytically and oxidatively stable and function in a variety of detergent formulations. The catalysts of the invention enhance the bleaching action of hydrogen peroxide bleaching agents and of organic and inorganic peroxyacid compounds.

A further surprising feature is that the bleach catalysts are compatible with detergent enzymes, such as proteases, cellulases, lipases, amylases, oxidases etc.

The bleach composition according to the invention are effective on a wide range of stains including both hydrophilic and hydrophobic stains.

Accordingly, in a further aspect, the invention provides a method of bleaching a stained substrate, the method comprising contacting the stained substrate in aqueous media with a bleaching agent selected from the group of peroxy compound bleaches including hydrogen peroxide, hydrogen peroxide-liberating or generating compounds, peroxyacids and their salts, and peroxyacid bleach precursors and mixtures thereof, and a manganese complex of formula (I), as hereinbefore defined, each in an effective amount to interact with one another and provide a cleaning effect upon the substrate.

The effective level of the complex, expressed in terms of parts per million (ppm) of the manganese in an aqueous bleaching solution, will normally range from 0.001 ppm to 100 ppm, preferably from 0.01 ppm to 20 ppm, most preferably from 0.1 ppm to 10 ppm. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp-bleaching. The lower levels quoted are primarily intended and preferably used in domestic laundry operations.

Compositions comprising a peroxy compound bleach and the bleach catalyst are effective over a wide pH range of between 7 and 13, with optimal pH range lying between 8 and 11.

As stated above, the peroxy bleach compounds which can be utilized in the bleaching composition and detergent bleach composition of the present invention include hydrogen peroxide, hydrogen peroxide-liberating compounds, hydrogen peroxide-generating systems, peroxyacids and their salts, and peroxyacid bleach precursor systems, and mixtures thereof.

Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates persilicates and persulphates. Mixtures of two or more of such compounds may also be used. Particularly preferred are sodium percarbonate and sodium perborate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred to sodium perborate tetrahydrate because of its excellent storage stability combined with its ability to dissolve very quickly in aqueous bleaching solutions. Sodium percarbonate may be preferred for environmental reasons.

Alkylhydroxy peroxides are another class of peroxide bleaching agents. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

Organic peroxyacids may also be suitable as the peroxide bleaching agent. Such materials normally have the general formula:

$$\mathrm{HOO}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\mathrm{Y}$$

wherein R is an alkylene or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or

$$\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OOH}$$

group or a quaternary ammonium group.

Typical monoperoxy acids useful herein include, for example.

i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-α-naphthoic acid;

ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxylauric acid, peroxystearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and

iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

Typical diperoxyacids useful herein include, for example:

iv) 1,12-diperoxydodecanedioic acid (DPDA);

v) 1,9-diperoxyazelaic acid;

vi) diperoxybrassilic acid; diperoxysebasic acid and diperoxyisophthalic acid;

vii) 2-decylperoxybutane-1, 4-dioic acid;

viii) 4,4'-sulphonylbisperoxybenzoic acid.

Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS).

All these peroxide compounds may be utilized alone or in conjunction with a peroxyacid bleach precursor. an advantage of using a peroxyacid bleach precursor is that it may improve the overall whiteness of white fabrics. Such materials may also be used because of the hygiene benefits they confer on materials treated therewith.

Peroxyacid bleach precursors are known and amply described in literature, such as in British Patents 836,988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; European Patent Specification Nos 0185522; 0174132 and 0120591; and US Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

Another useful class of peroxyacid bleach precursors are the quaternary ammonium substituted peroxyacid precursors disclosed in US Patents 4,751,015 and 4,397,757, and in European Patent Specification Nos 284,292, 331,229 and 303,520. Examples of peroxyacid bleach precursors of this class are:
2-(N,N,N-trimethyl ammonium) ethyl-4-sulphophenyl carbonate - (SPCC);
N-octyl,N,N-dimethyl-N10-carbophenoxy decyl ammonium chloride - (ODC);
3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and
N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

A further special class of cationic peroxyacid bleach precursors is formed by the cationic nitriles as disclosed in European Patent Specification No 303520, 458396 and 464880.

Any one of these peroxyacid bleach precursors may be used in the present invention. Of the above classes of bleach precursors, the preferred materials are esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoloxy benzene sulphonate (SBOBS); N,N,N'N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoloxy benzoate; SPCC; trimethyl ammonium toluyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyloxybenzene

sulphonate (STHOBS); and th substituted cationic nitriles.

Particularly suitable materials are the so-called sulphonimides as disclosed in European Patent Specification Nos 453,003 and 446,982.

A detergent bleach composition of the invention can be formulated by combining effective amounts of the components. The term "effective amounts" as used herein means the components are present in quantitites such that each of them is operative for its intended purpose when the resulting mixture is combined with water to form an aqueous medium which may be used to wash and clean clothes, fabrics and other articles.

In particular, the detergent bleach composition can be formulated to contain, for example, from about 2% to 30% by weight, preferably from 5 to 25% by weight, of a peroxide compound.

Peroxyacids may be used in somewhat lower amounts, for example from 1% to about 15% by weight, preferably from 2% to 10% by weight.

Peroxyacid precursors may be used in combination with a peroxide compound at approximately the same level as peroxyacids, i.e. 1% to 15%, preferably from 2% to 10% by weight.

The complex will be present in the bleach and detergent bleach compositions in amounts so as to provide the required level of in the wash liquor. Normally, the manganese content in the formulation is from 0.0005% to about 0.5% by weight, preferably 0.001% to 0.25% by weight.

When used in a detergent bleach composition to be dosed at low levels, for example by Japanese and US consumers at dosages of about 1 and 2 g/l respectively the Mn content in the formulation is at 0.0025 to 0.5% by weight, preferably 0.005 to 0.25%. At higher product dosages as used, for example, by European consumers, the Mn content in the formulation is from 0.0005 to 0.1% by weight, preferably from 0.001 to 0.05%.

The bleach catalyst of the invention is compatible with substantially any known and common surface-active agents and detergency builder materials.

The surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The total level of the surface-active material may be from 0.5% up to 50% by weight, and is preferably from about 1% to 40% by weight of the composition, most preferably 4 to 25% by weight.

Synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl groups containing from about 8 to 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl groups.

Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those esters of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C_9-C_{18}) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulphonate; sodium and ammonium C_7-C_{12} dialkyl sulfosuccinates; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C_{11}-C_{15}) alkylbenzene sulphonates, sodium (C_{16}-C_{18}) alkyl sulphates and sodium (C_{16}-C_{18}) alkyl ether sulphates.

Examples of suitable nonionic surface-active compounds which may be used include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6-C_{22}) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; the condensation products of aliphatic (C_8-C_{18}) primary, secondary linear or branched alcohols with ethylene oxide, generally 3-30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene diamine. Other so-called nonionic surface-actives include alkyl polyglycosides, long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Amounts of amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If amphoteric or zwitterionic detergent compounds are used it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

As stated above, soaps may also be incorporated in the compositions of the invention. However, the bleach

performance of the bleaching and detergent bleach composition is improved if the amount of long-chain C_{16} - C_{22} fatty acid soaps is kept to a minimum. Short chain C_{12} - C_{14} fatty acid soaps may be included preferably at levels not more than about 10% by weight.

High levels of anionic surfactant are also believed to reduce bleach performance to below optimum levels.

Preferably the detergent bleach composition comprises a surface-active material, a peroxide bleaching agent, a complex of general formula (I) as hereinbefore defined, 0 to 25% by weight of anionic surfactant and 7.5 to 55% by weight of nonionic surfactant, the weight ratio of nonionic surfactant to anionic surfactant being at least 0.75.

The detergent bleach composition of the invention will normally also contain a detergency builder. Builder materials may be selected from calcium sequestrant materials; precipitating materials; calcium ion-exchange materials and mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of ether polycarboxylates, such as carboxymethyloxy succinic acid, oxydisuccinic acid, mellitic acid; ethylene diamine tetraacetic acid; benzene polycarboxylic acids; citric acid; and polyacetal carboxylates as described in US Patents 4,144,226 and 4,146,495.

Examples of precipitating builder materials include sodium orthophosphate, sodium carbonate and sodium carbonate/ calcite.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are well-known examples.

In particular, the compositions of the invention may contain any one of the organic or inorganic builder materials, such as sodium or potasssium tripolyphosphate, sodium or potassium pyrophosphate, sodium or potassium orthophosphate, sodium carbonate or sodium carbonate/calcite mixtures, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyl malonate, carboxymethyloxy succinate and the water-insoluble crystalline or amorphous aluminosilicate builder materials, or mixtures thereof.

If a phosphate builder is used, preferably a peroxyacid is present as the bleach agent.

The builder materials may be present at a level of, for example, from 5 to 80% by weight, preferably from 10 to 60% by weight.

The detergent compositions of the invention may also contain conventional additives in the amounts at which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers, such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids, lather depressants, such as alkyl phosphates and silicones, anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers, other stabilizers, such as ethylene diamine tetraacetic acid (EDTA) and the phosphonic acid derivatives (i.e. Dequest ^{R} types), fabric softening agents, inorganic salts, such as sodium sulphate, and, usually present in very small amounts, fluorescent agents, perfumes, enzymes, such as proteases, cellulases, lipases, amylases and oxidases, germicides and colourants.

Of these additives, transition metal sequestrants, such as EDTA and the phosphoric acid derivatives, e.g. ethylene diamine tetra-(methylene phosphonate) EDTMP are particularly important.

Another optional but highly desirable additive with multi-functional characteristics is a polymeric material having a molecular weight of from 1,000 to 2,000,000 and which can be a homo- or co-polymer of acrylic acid, maleic acid, or salt or anhydride thereof, vinyl pyrrolidone, methyl-or ethyl-vinyl ethers, and other polymerisable vinyl monomers. Preferred examples of such polymeric materials are polyacrylic acid or polyacrylate; polymaleic acid/acrylic acid copolymer; 70:30 acrylic acid/hydroxyethyl maleate copolymer; 1:1 styrene/maleic acid copolymer; isobutylene/maleic acid and diisobutylene/ maleic acid copolymers; methyl- and ethylvinylether/ maleic acid copolymers; ethylene/maleic acid copolymer; polyvinyl pyrrolidone; and vinyl pyrrolidone/maleic acid copolymer. Such a polymeric additive is usually present at a level from about 0.1% to about 3% by weight.

When using a hydroperoxide, such as sodium perborate or sodium percarbonate, as the bleaching agent, it is preferred that the composition contains not more than 5% by weight of carbonate, expressed as sodium carbonate, more preferably not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Detergent bleach compositions of the invention, when formulated as free-flowing particles, e.g. in powdered or granulated form, can be produced by any of the conventional techniques employed in the manufacture of detergent compositions, for instance by slurry-making, followed by spray-drying, to form a detergent base powder to which heat-sensitive ingredients including the peroxy compound bleach, conventional additives, and the complex can be added as dry substances.

It will be appreciated, however, that the detergent base powder compositions, to which the complex is add-

ed, can itself be made in a variety of other ways, such as the so-called part-part processing, non-tower route processing, dry-mixing, agglomeration, granulation, extrusion, compacting and densifying processes etc., such ways being well known to those skilled in the art and not forming an essential part of the present invention.

Alternatively, the complex may be added separately to a wash/bleach water containing the peroxy bleaching agent.

In that case, the complex is included as a detergent additive product. Such additive products are intended to supplement or boost the performance of conventional detergent compositions and may contain any of the components of such compositions, although they will not comprise all of the components present in a fully formulated detergent composition. Additive products in accordance with this aspect of the invention will normally be added to an aqueous liquor containing a source of (alkaline) hydrogen peroxide, although in certain circumstances the additive product may be used as separate treatment in a pre-wash or in the rinse.

Additive products in accordance with this aspect of the invention may comprise the complex alone or, preferably, in combination with a carrier, such as a compatible aqueous or non-aqueous liquid medium or a particulate substrate or a flexible non-particulate substrate.

Examples of compatible particulate substrates include inert materials, such as clays and other aluminosilicates, including zeolites, both of natural and synthetic origin. Other compatible particulate carrier materials include hydratable inorganic salts, such as carbonates and sulphates.

The complex can also be formulated in detergent bleach compositions of other product forms, such as flakes, tablets, bars and liquids and particularly non-aqueous liquid detergent compositions.

Such non-aqueous liquid detergent compositions in which the complex may be incorporated are known in the art and various formulations have been proposed, e.g. in US Patents 2,864,770; 3,368,977; 4,772,412; GB Patents 1,205,711; 1,370,377; 2,914,536; DE-A-2,233,771 and European Patent Specification No. 0,028,849.

These are compositions which normally comprise a non-aqueous liquid medium, with or without a solid phase dispersed therein. The non-aqueous liquid medium may be a liquid surfactant, preferably a liquid nonionic surfactant; a non-polar liquid medium, e.g. liquid paraffin; a polar solvent, e.g. polyols, such as glycerol, sorbitol, ethylene glycol, optionally combined with low-molecular monohydrix alcohols, e.g. ethanol or isopropanol; or mixtures thereof.

The solid phase can be builders, alkalis, abrasives, polymers, clays, other solid ionic surfactants, bleaches, fluorescent agents and other usual solid detergent ingredients.

The invention will now be illustrated by way of the following example:

Example I

The following examples were carried out in glass vessels, equipped with a temperature controlled heating spiral in quartz, magnetic stirrer, thermo-couple and pH electrode.

At 40°C isothermal, experiments in demineralised water at pH 10, were carried out to determine the bleach performance of sodium perborate monohydrate (PBM) and a mononuclear complex as bleach catalyst on standard tea-stained test cloths.

The bleach system in the wash solution was added at a concentration of 8.6 mmol/l PBM which corresponds to 14.3% by weight of PBM if a detergent bleach formulation is dosed at 6g/l.

Test cloths were immersed for 30 minutes in each of the compositions of the examples. After rinsing with tap water, the cloths were dried in a tumble drier. The reflectance (R_{460*}) was measured on a Zeiss Elrephometer before and after treatment. The difference (ΔR_{460*}) in the value gives a measure of the effectiveness of the treatment.

The results are shown in the following Table I.

TABLE I

		ΔR
(A)	Blank (no catalyst)	5.5
(B)	+ Free $Mn(NO_3)_2$ (5×10^{-6} mol/l	12.0
(C)	+ $[Mn_2^{IV}(\mu\text{-}O)_3(1,4,7\text{-}Me_3TACN)_2]$ $(PF_6)_2$ (2.5×10^{-6} mol/l	25.1
I	+ $[1,4,7\text{-}Me_3TACN.Mn^{III}Cl_3]$ (5×10^{-6} mol/l	26.3
II	+ $[1,4,7\text{-}Me_3TACN.Mn^{II}(NH_3)_3]^{2+}$ (5×10^{-6} mol/l)	25.3
III	+ $[1,4,7\text{-}Me_3TACN\ Mn^{III}\ (N_3)_3]$ (5×10^{-6} mol/l)	22.0
IV	+ $[1,4,7\text{-}Me_3TACN\ Mn^{III}(SCN)_3]$ (5×10^{-6} mol/l)	25.0
V	+ $[1,4,7\text{-}Me_3TACN$ Mn (AcAc) (EtO)] BPh_4 (5×10^{-6} mol/l dissolved in 5 ml of ethanol and added to 995 ml of bleach solution containing PBM)	26.0

The level of mononuclear Mn complex corresponds to 0.03% by weight of catalyst if a detergent composition is dosed at 6 g/l.

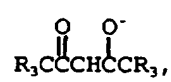
Experiments (A), (B), and (C) were used as controls. The above results clearly show that the mononuclear manganese coordination complexes (2), (3), (4), (5) and (7) were at least as effective as the preferred dinuclear complex catalyst $[Mn_2^{IV}(\mu\text{-}O)_3(1,4,7\text{-}Me_3TACN)_2](PF_6)_2$, described in EP-A-458 397 and EP-A-458 398.

Claims

1. A bleach catalyst comprising a complex of formula (I):

$$[L\,MnX_p]^zY_q \qquad (I)$$

wherein:-
Mn is manganese in the II, III or IV oxidation state; X represents a coordinating species selected from Cl^-, Br^-, I^-, F^-, NCS^-, I_3, ^-OH, O_2^{2-}, O^{2-}, HOO^-, H_2O, SH, CN^-, OCN^-, S_4^{2-}, NH_3, NR_3, $RCOO^-$, RO^-,



RSO_3^- and RSO_4^- in which R is selected from hydrogen, alkyl, aryl, both optionally substituted, and $R'COO^-$ where R' is selected from alkyl and aryl, both optionally substituted; and mixtures thereof;
p is an integer from 1 to 3;
z is the charge of the complex and is an integer which can be positive, negative or zero;
y is a counterion, the type of which is dependent upon z;
q = z/[charge Y]; and
L is a ligand which is a macrocyclic organic molecule of formula

$$\left[NR^3-(CR^1(R^2)_u)_t \right]_s$$

where
t is an integer from 2 to 3;
s is an integer from 3 to 4;
u is zero or one; and
R^1, R^2 and R^3 are each independently selected from hydrogen, alkyl and aryl, both optionally substituted; with the proviso that when p is 3 and Mn is manganese in the IV oxidation state X cannot each be RO^-.

2. A bleach catalyst according to claim 1 wherein in the ligand L t is 2, s = 3, u = 1 and R^1, R^2 and R^3 are

each independently hydrogen or methyl.

3. A bleaching composition comprising:
   i) from 2 to 30% by weight of a peroxy compound; and
   ii) a bleach catalyst as claimed in claim 1, present in an effective amount for catalysing bleaching activity of the peroxy compound.

4. A bleaching composition according to claim 3 comprising a bleach catalyst at a level corresponding to a manganese content of from 0.0005 to 0.5% by weight based on the composition.

5. A bleaching composition according to claims 3 or 4 further comprising a surface-active material in an amount from 0.5 to 50% by weight.

6. A bleaching composition according to anyone of claims 3 to 5 further comprising a detergency builder in an amount from 5 to 80% by weight.

7. A method of bleaching a stained substrate the method comprising contacting the stained substrate in aqueous media with a peroxy compound and a manganese complex each in an effective amount to interact with one another and provide a cleaning effect upon the substrate, the complex having the formula (I):

$$[L\,MnX_p]^z Y_q \qquad (I)$$

wherein:-
Mn is manganese in the II, III or IV oxidation state;
X represents a coordinating species selected from Cl^-, Br^-, I^-, F^-, NCS^-, I_3, ^-OH, O_2^{2-}, O^{2-}, HOO-, H_2O, SH, CN^-, OCN^-, S_4^{2-}, NH_3, NR_3, $RCOO^-$, RO^-,

RSO_3^- and RSO_4^- in which R is selected from hydrogen, alkyl, aryl, both optionally substituted, and $R'COO^-$ where R' is selected from alkyl and aryl, both optionally substituted, and mixtures thereof;
p is an integer from 1 to 3;
z is the charge of the complex and is an integer which can be positive, negative or zero;
y is a counterion, the type of which is dependent upon z;
q = z/[charge Y]; and
L is a ligand which is a macrocyclic organic molecule of formula

$$[NR^3\text{-}(CR^1(R^2)_u)_t]_s$$

where
t is an integer from 2 to 3;
s is an integer from 3 to 4;
u is zero or one; and
R^1, R^2 and R^3 are each independently selected from hydrogen, alkyl and aryl, both optionally substituted; and
with the proviso that when p is 3 and Mn is manganesee in the IV oxidation state X cannot each be RO^-.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 31 1580

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,D	EP-A-0 458 397 (UNILEVER NV ET AL.) * page 3 - page 5 *	1-7	C11D3/39 C07F13/00
A	EP-A-0 292 689 (E.R.SQUIBB & SONS, INC) * claims 29,34,64 *	1	
A	EP-A-0 414 581 (S.A.CAMP FABRICA DE JABONES) * page 4, line 43 - line 58 * * claims 1,2 *	1,3	
A	EP-A-0 443 651 (UNILEVER NV ET AL.) * claims; examples *	1,3	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C11D
C07F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	15 MARCH 1993	PELLI-WABLAT B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document